PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2000-251533

(43)Date of publication of application : 14.09.2000

(51)Int.Cl.
H01B 1/08
B01D 53/22
B01D 71/02
G01N 27/409
H01G 4/33
H01J 17/06
H01M 4/86

(21)Application number : 11-046552

(22)Date of filing : 24.02.1999

(71)Applicant : MITSUBISHI MATERIALS CORP

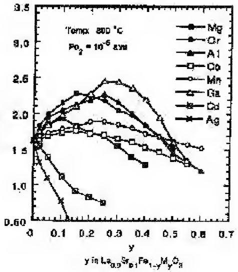
(72)Inventor : AKIKUSA JUN
KOMADA KIICHI

(54) OXIDE-ION MIXED CONDUCTOR AND ITS APPLICATION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a relatively inexpensive air electrode material for a solid- oxide-type fuel cell.

SOLUTION: This oxide-ion mixed conductor has a composition represented by a formula La1-x Srx Fe1-yMyO3, where x is 0.02-0.50, M is one or more of Mg, Cr, Al, Ga, y is 0.02-0.25 for M=Mg, 0.02-0.50 for M=Cr, 0.02-0.45 for M=Al, 0.02-0.50 for M=Ga, and total of ys is not more than 0.55 for two or more Ms. This oxide-ion mixed conductor has a perovskite-type structure showing a constant and high electric conductivity in a temperature range of 500-1000°C.



CLAIMS

[Claim(s)]
[Claim 1]A general formula: A perovskite type oxide ion mixed conductor with a presentation shown by $La_{1-x}Sr_xFe_{1-y}M_yO_3$. x is 0.02-0.50 among a formula, and M is one sort of Mg, Cr, aluminum, and Ga, or two sorts or more, :M=Mg whose y is as follows per M elements each however whose total value of y in case M is two or more sorts is 0.55 or less, y= 0.02 to 0.25, M=Cr, y= 0.02 to 0.50, M=aluminum, y= 0.02 to 0.45, M=Ga, y= 0.02-0.50.
[Claim 2]A solid oxide type fuel cell having an air pole containing the oxide ion mixed conductor according to claim 1.
[Claim 3]The solid oxide type fuel cell according to claim 2 with which an electrolyte consists of an oxide ionic conductor shown with a following general formula.
$Ln_{1-x'}A_{x}$ -- $Ga_{1-y'-'z'}$ -- among a $B1_{y'}B\text{-}2_{z'}O_3$ type, One sort or two sorts or more of Ln=La, Ce, Pr, Nd, and Sm; one sort or two sorts or more of one sort or two or more sort;B-2=Co of one-sort or two or more sort;B1=Mg of A=Sr, Ca, and Ba, aluminum, and In, Fe, nickel, and Cu;
x'=0.05-0.3 ;
y'= 0.025-0.29;
z'=0.01-0.15;
y'+z'<=0.3.
[Claim 4]A gas separation membrane consisting of the oxide ion mixed conductor according to claim 1.
[Claim 5]A solid oxide type gas sensor having an electrode containing the oxide ion mixed conductor according to claim 1.
[Claim 6]A gas discharge type display panel having the negative pole containing the oxide ion mixed conductor according to claim 1.
[Claim 7]An element for solid oxide type emission gas purification having a thin film which becomes a cathode surface from the oxide ion mixed conductor according to claim 1.

[Claim 8]A thin film capacitor having a thin film electrode which consists of the oxide ion mixed conductor according to claim 1.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to the new oxide ion mixed conductor which takes perovskite type structure. The oxide ion mixed conductor concerning this invention shows the conductivity by the high electronic-oxide ion mixed conduction fixed in the wide temperature requirement, and is an electrode of a fuel cell. (air pole) Including, it is useful for various kinds of uses.
[0002]
[Description of the Prior Art]Oxide ion mixed conductors are electron nature electrical conduction and oxide ion. (O^{2-}) It is the material in which both of the ionicity electrical conduction to depend contribute, and electrical conductivity is shown. If electron nature conductivity of such a material is made into $sigma_e$ and ionicity conductivity is made into $sigma_i$, $sigma_i/(sigma_e+sigma_i)$ Values are the ion transference number and $sigma_e/(sigma_e+sigma_i)$. A value is the electronic transference number and it is conductivity, respectively. $(sigma_e+sigma_i)$ It is the rate of ionicity electrical conduction and electron nature electrical conduction of occupying. This ion transference number. A mixed conductor can be considered if it is within the limits of 0.1-0.7. If higher as an electronic conductor than 0.7 when the ion transference number is lower than 0.1, it will be treated as an oxide ionic conductor.
[0003]There was almost no material outstanding until now in an oxide ion mixed conductor. For example, CeO_2 which made Y_2O_3, Gd_2O_3, or CaO dissolve is an oxide ionic conductor in an oxidizing atmosphere. (that is, oxide ion conductivity is dominant) Although it is, In the reducing atmosphere, n type electron nature electrical conduction appearing by change of Ce^{4+}->Ce^{3+}, and the ion transference number falling, and becoming a mixed conductor is known. This

character is used and it is a fuel electrode of a solid oxide type fuel cell (SOFC). (anode) Using it was examined. However, there is a problem that crystalline-lattice volume changes with atmosphere a lot.

[0004]Although the material in which mixed conductivity is shown according to a reducing atmosphere was known as mentioned above, the material in which the mixed conductivity excellent also in the oxidizing atmosphere is shown was hardly known until now. If there is such a material, it will be an air pole of a solid oxide type fuel cell. (cathode) It is useful.

[0005]The air pole of a solid oxide type fuel cell is chemically stable under hot 10^{-15} - the atmosphere of the oxygen tension beyond 10^{-10} atmospheric pressure grade, and needs to consist of materials in which high electron nature electrical conduction is moreover shown. Since common metal cannot be used, the conductive perovskite type oxide has been used. The conventional air pole material is a material mainly shown by $La_{1-x}A_xBO_3$ (A is Ca and B is [Sr or] Mn or Co). This kind of material is a material in which electron nature electrical conduction is mainly shown, since ionicity electrical conduction is very small, it is restricted an air pole, an electrolyte, and near the three-phase-circuit interface of air, polarization in an air pole becomes large, and it has become a cause by which the output of a cell declines so that an electrode reaction may mention later.

[0006]Its attention is paid to the high conductivity about $La_{1-x}Sr_xMO_3$ (M is one sort of Co, nickel, Fe, Mn, and Cu, or two sorts or more) which is a perovskite type oxide which includes some above-mentioned materials, Various kinds of uses are proposed until now besides the above-mentioned air pole.

[0007]For example, JP,4-366523,A and 5-74352 Gas discharge type display panel ** which equipped the **** gazette with the negative pole formed from the mixture of this material and insulating material is proposed. In JP,4-298240,A, using the mixture of this material and platinum for the electrode of a solid oxide type oxygen sensor or the air pole of a fuel cell is indicated. In JP,9-299749,A, the element for emission gas purification which formed the electrode in both sides of a solid electrolyte element, and formed the oxide film which consists of the above-mentioned material on the cathode terminal is indicated.

[0008]

[Problem(s) to be Solved by the Invention]Let it be a technical problem to provide the comparatively cheap oxide ion mixed conductor which shows good electronic-oxide ion mixed conductivity over a temperature requirement as wide as not less than 1000 ** from this invention and 500-600 **, and has the outstanding performance with high conductivity and the small temperature change which is not in the former.

[0009]

[Means for Solving the Problem]This invention persons found out that $La_{1-x}Sr_xFeO_3$ showed

good oxide ion mixed conductivity in a process in which research of a perovskite type oxide ionic conductor is advanced. And when a part of Fe of B site of this material was replaced by one sort of Mg, Cr, aluminum, and Ga, or two sorts or more, that conductivity improved and it found out that an aforementioned problem was solvable.

[0010]This invention is a following general formula (a) here. :$La_{1-x}Sr_xFe_{1-y}M_yO_3$ which is a perovskite type oxide ion mixed conductor with a presentation shown ... x is 0.02-0.50 among the (a) above-mentioned type, M is one sort of Mg, Cr, aluminum, and Ga, or two sorts or more, and the y is as follows per M elements each, however, : whose total value of y in case M is two or more sorts is 0.55 or less -- M=Mg, y= 0.02 to 0.25, M=Cr, y= 0.02 to 0.50, M=aluminum, y= 0.02 to 0.45, M=Ga, and y= 0.02-0.50.

[0011]very high conductivity fixed in a wide temperature requirement which reaches more than 1000 ** or it from material of this invention, and 500-600 ** (an example.) 100 - 300 Scm^{-1} is shown, and the ion transference number It is within the limits of 0.1-0.3, and fully functions as an oxide ion mixed conductor.

[0012]A solid oxide type fuel cell which has again an air pole containing the above-mentioned oxide ion mixed conductor according to this invention, A gas separation membrane which consists of the above-mentioned oxide ion mixed conductor, a solid oxide type gas sensor which has an electrode containing the above-mentioned oxide ion mixed conductor, A thin film capacitor which has an electrode of a thin film which consists of an element for solid oxide type emission gas purification which has a gas discharge type display panel which has the negative pole containing the above-mentioned oxide ion mixed conductor, and a thin film which consists of the above-mentioned oxide ion mixed conductor in a cathode surface, and the above-mentioned oxide ion mixed conductor is also provided.

[0013]

[Embodiment of the Invention]The oxide ionic conductor of this invention has a Perovskite type crystal structure, Ln and Sr occupy A site of the perovskite type crystal shown by ABO_3, and Fe and M element occupy the B site.

[0014]Originally, when Sr of divalent metal occupies a part of A site among A and the B car sites which trivalent metal occupies and Fe which can take divalent metal and/or divalent, and trivalent occupies at least a part of B site, an oxygen hole is produced and oxide ion conductivity arises by this oxygen hole. Therefore, since only the part of this oxygen hole decreases, the number of oxygen atoms is a general formula (a). The number of oxygen atoms which can be set is actually smaller than three. However, since it is difficult to display the number of oxygen atoms correctly, it is a general formula (a) for convenience. The number of oxygen atoms is then displayed as 3.

[0015](a) M element is not included in a formula. (namely, y= 0) Material, i.e., $La_{1-x}Sr_xFe_{1-y}O_3$,

is indicated to JP,4-298240,A, for example, and it is publicly known. However, it is not recognized until now that this material is an oxide ion mixed conductor.
[0016]x value and conductivity of this $La_{1-x}Sr_xFe_{1-y}O_3$ (sigma) Relation (measuring condition: temperature 800 **, oxygen tension 10 $^{-5}$ atm) To drawing 1, they are x value and the ion transference number. (temperature 800 **) A relation is shown in drawing 2, respectively. Addition of drawing 1 to Sr (increase in x value) Conductivity increases greatly and it turns out that increase of the conductivity accompanying [in especially x] the increase in x value at the range of 0.02-0.1 is large. From drawing 2, if x value becomes large, the ion transference number will fall gradually, but the ion transference number of x is [0.50] 0.1. It turns out that the above is held. Therefore, as for this material, it turns out that x is an oxide ion mixed conductor which has high conductivity in 0.02-0.50.
[0017]The material concerning this invention replaces a part of Fe of the material shown in drawing 1 by M element. Atomic ratio of this M element (y value of the aforementioned (a) formula) Relation with conductivity (a measuring condition is the same as drawing 1) It is shown in drawing 3. Conductivity increases remarkably that M element is Mg, Cr, aluminum, or Ga according to this invention with increase of y value, and conductivity can be improved by addition of a little M elements so that drawing 3 may show.
[0018]Although some conductivity, on the other hand, increases with the addition that M element is Co or Mn, if the increase is small and these expensive elements are not added comparatively so much (if y value does not become large) The conductivity which increased cannot be obtained. By Ag or Cd, conductivity will fall [M element] remarkably with addition of M element conversely. Therefore, from this figure, when M elements are Mg, Cr, aluminum, and Ga, it restricts, the remarkable improvement in conductivity is found by a little addition -- it turns out that it becomes possible to obtain cheaply the conductive perovskite type oxide material in which very high conductivity called 100 - 300 Scm^{-1} is shown.
[0019]It is based on the knowledge shown in this drawing 1 - drawing 3, and is (a). The kind of x in a formula, y, and M element was determined. That is, if x value is smaller than 0.02, conductivity will fall remarkably (refer to drawing 1). If x value is higher than 0.50, the ion transference number will come (refer to drawing 2) to be less than 0.1. It stops functioning as an oxide ion mixed conductor. x value is 0.3 so that using 0.05 or more if the improved effect of conductivity is taken into consideration may secure as high the ion transference number as possible about a maximum preferably. Carrying out the following is preferred. More desirable x value is within the limits of 0.08-0.25.
[0020]About y value, since the action of change of the conductivity to y value changed with kinds of M element, the range of y value was determined that an improvement of significant conductivity is obtained compared with the case of y= 0 as mentioned above for every M

element from drawing 3. If it separates from the range of y value of each element, increase of the significant conductivity in comparison with the case of y= 0 will not be acquired. The range with preferred y value is as follows.
[0021]M=Mg, y= 0.05 to 0.15, M=Cr, y= 0.10 to 0.30, M=aluminum, y= 0.15 to 0.30, M=Ga, y= 0.20-0.40.
[0022]The temperature dependence of the conductivity of the material concerning this invention is shown in drawing 4. Drawing 4 is low temperature, so that the value of the horizontal axis is large, and it is specifically a plot at each temperature of 1000 **, 900 **, 800 **, 700 **, 600 **, and 500 ** from the left. At a $LaSrFeMO_3$ system, it is at least to some conductivity falling, if temperature becomes low in $LaFeO_3$ as shown in this figure. Regardless of conductivity, it is fixed to a temperature change in the temperature requirement of 500 - 900 **. Therefore, there is an advantage that the oxide ion mixed conductor of this invention has the dramatically small temperature dependence of conductivity, it is mostly fixed and every temperature shows the very high conductivity.
[0023]If temperature dependence of conductivity is large and temperature falls in ionicity electrical conduction material in many cases, usually conductivity also falls. Therefore, to the electrical conductivity of the perovskite die materials of this invention this indicates the temperature change of different conductivity to be, it is possible that not only the ionicity electrical conduction by oxide ion but electron nature electrical conduction has contributed considerably.
[0024]In order to confirm this point, the result of having measured the ion transference number of the material concerning this invention at the temperature which changes with methods of a statement in the example which measures the electromotive force of an oxygen concentration cell, and which is mentioned later is shown in drawing 5.
[0025]As shown in drawing 5, as for the material of this invention, the ion transference number increases as temperature rises from 450 ** to 800 **, at an elevated temperature, increase of the ion transference number becomes small from 800 **, or the action that the ion transference number falls a little conversely is shown. as mentioned above, ionicity electrical conduction falls with a temperature fall, but with the material of this invention, if temperature falls, the ion transference number falls, and since the rate of electrical conductivity becomes large, it will be thought that the conductivity carried out about 1 law regardless of temperature is shown. Since the ion transference number becomes lower than 0.1 by the low temperature side depending on the kind of M element, when using it as an oxide ion mixed conductor, the ion transference number is service temperature 0.1 It is set as the temperature which becomes the above.
[0026]The oxide ion mixed conductor of this invention fabricates suitably by a means the mixture which mixed the powder of each oxide of a constituent element well by the predetermined blending ratio, and can manufacture it by making it sinter. Catalyst precursor

which carries out a pyrolysis during calcination and becomes an oxide as the end of precursor powder in addition to an oxide (an example, carbonate, carboxylate, etc.) It can be used. Not less than 1100 ** of calcination temperature for sintering is not less than 1200 ** preferably, and firing time is several hours thru/or tens of hours. In order to shorten firing time, preliminary calcination of the raw material mixture may be carried out at low temperature from sintering temperature. This preliminary calcination can be carried out by heating at 500-1200 ** for about 1 to 10 hours, for example. After grinding the mixture which carried out preliminary calcination if required, it is fabricated and is made to sinter eventually. The shaping can adopt proper powder molding means, such as uniaxial pressing, a hydrostatic pressure press, extrusion molding, and tape cast shaping. Firing environmentses also including preliminary calcination have preferred oxidizing atmospheres or inert gas atmospheres, such as air.

[0027]General formula (a) of this invention The oxide ion mixed conductor shown, Since B site consists of mainly cheap Fe, in spite of being comparatively cheap, it is an oxide ion mixed conductor in which conductivity with expensive high $LaCoO_3$ of material cost, $LaMnO_3$, and the level is shown, and oxide ion conductivity is moreover also shown in addition to electron conductivity. Therefore, this material is an electrode of a solid oxide type fuel cell (SOFC), especially an air pole. (cathode) It is useful as a material and the fall of the manufacturing cost of a solid oxide type fuel cell is expected. Other elements of a fuel cell in that case, i.e., an electrolyte and a fuel electrode, (anode) Material in particular is not restricted. For example, as an electrolyte, the stabilized zirconia mainly used from before, especially yttria stabilized zirconia (YSZ) can be used. Besides a Ni metal, the fuel electrode can also use cermets, such as nickel-YSZ and nickel-CeO_2.

[0028]In SOFC which makes an air pole the oxide ion mixed conductor of this invention, especially the material of a desirable electrolyte and a fuel electrode is as follows.

[0029]A desirable electrolyte material is a following general formula (b). It is an oxide ionic conductor which consists of a perovskite type oxide shown.

[0030]

$Ln_{1-x'z[}A_{x'}Ga_{1-y'-]'}B1_{y'}B\text{-}2_{z'}O_3$ ... Inside of the (b) type, One sort or two sorts or more of Ln=La, Ce, Pr, Nd, and Sm; one sort or two sorts or more of one sort or two or more sort;B-2=Co of one-sort or two or more sort;B1=Mg of A=Sr, Ca, and Ba, aluminum, and In, Fe, nickel, and Cu;

x'=0.05-0.3 ;

y'= 0.025-0.29;

z'=0.01-0.15;

y'+z'<=0.3.

[0031]This oxide is a thing of the same Perovskite type crystal structure as an oxide ion mixed

conductor suitable for the air pole of this invention. This general formula (b) In the oxide shown, two kinds of dope elements, B1 and B-2, are contained to B site, and it is 2. What is necessary is just to choose B-2 element according to the operating temperature of SOFC, since conductive temperature characteristics change with the kinds of element. For example, in performing turbine power generation by exhaust gas simultaneously as cogeneration. Since the high operating temperature of around 1000 ** is preferred, it is preferred that B-2 atom in which such ionicity electrical conduction high at an elevated temperature is shown uses for an electrolyte Co and Fe, and 5 element-system oxide that is especially Co. On the other hand, if operating temperature is an 800 ** grade, B-2 atom can use what is nickel in addition to the above, and if operating temperature is below 600 ** further, B-2 atom can use what is Cu.
[0032]The voltage drop of SOFC by electrolytic resistance loss is large, and high power is obtained for a thin film. Therefore, electrolytic YSZ is used with an about 30-50-micrometer thin film. However, since the oxide ion conductivity of YSZ is small still in addition, in order to obtain practically sufficient performance, it is necessary to heat at about 1000 **. It is reported with the thin film YSZ of 30 micrometers of thickness thickness that the practical power density at the operating temperature of 1000 ** is a 0.35 W/cm^2 grade. In order to make the output of a cell higher than this or to make operating temperature low, the example of an experiment which uses the YSZ thin film of the thinness of several micrometers thru/or about 10 micrometers is reported, but the gas impermeability for which an electrolyte is asked in such a thin film becomes uncertain, and is not desirable in respect of reliability.
[0033]General formula (b) The above-mentioned 5 element-system oxide shown, In order for a wide temperature requirement to show high oxide ion conductivity more remarkable than YSZ, even when SOFC is constituted using the electrolyte of the thick film which can be manufactured, for example with the sintering process of thickness 0.5 mm (= 500 mum), an output higher than the above-mentioned YSZ thin film can be obtained. Although it changes also with the kinds and atomic ratios of B-2 atom, compared with SOFC using the YSZ thin film of 30-micrometer thickness, even the operating temperature of 1000 ** endures this, and the maximum output density in this case is several times at operating temperature 800 **. (an example, 3 times, or more than it) It becomes large. If an electrolyte is thickened, the mechanical strength and life of a fuel cell will improve substantially. Or if the electrolyte which consists of the above-mentioned 5 element-system oxide is used by the film of thickness abbreviation 200 mum, in the low temperature 600 ** thru/or 700 **, power density equivalent to the YSZ film of 30-micrometer thickness demonstrating at 1000 ** can be obtained.
[0034]General formula (b) Since the oxide ionic conductor shown has the wide temperature requirement which shows high oxide ion conductivity, it can extend the operating temperature of SOFC. For example, when performing turbine power generation by exhaust gas simultaneously as cogeneration, the high operating temperature of around 1000 ** is preferred.

However, for example Since power generation by the exhaust gas of a steam or others can be simultaneously performed also with operating temperature with a low 600 - 700 ** grade, the generation efficiency of SOFC does not fall so much. Thus, when operating temperature becomes low, ferrous materials, such as stainless steel, can be used for the structural material of SOFC, and there is also an advantage that a material cost decreases remarkably compared with a material called nickel-Cr alloy and ceramics in case operating temperature is around 1000 **. Although SOFC operated at such low temperature was not able to be built in the conventional YSZ, according to this invention, it becomes possible [an elevated-temperature operation type] from such a low temperature operation type to build various SOFC(s) according to an operating environment.

[0035]It is the above-mentioned general formula (b) about an electrolyte. When constituted from a 5 element-system oxide shown, both an electrolyte and an air pole will comprise same perovskite type oxide material. On the other hand, in the conventional SOFC, an electrolyte and an air pole are YSZ(s) of a fluorite type [[/, for example an electrolyte, / which comprises a material of a different kind in which crystal structures differ], and an air pole is perovskite type La(Sr) CoO_3]. . In this case, if it sees microscopically with an atom level, the very thin volume phase which the material of both layers produces in response to the interface of an electrolyte and an air pole will generate, and an output will decline for the voltage loss by that interfacial resistance. By constituting an electrolyte and an air pole from a material of the same kind, even if a volume phase generates, interfacial resistance becomes small.

[0036]Since in addition to the problem of interfacial resistance both coefficients of thermal expansion differ when an electrolyte and an air pole are materials of a different kind, the heat stress added at the time of temperature up and a temperature fall becomes large. This problem is also remarkably reduced by constituting an electrolyte and an air pole from a material of the same kind.

[0037]Above-mentioned interfacial resistance and heat stress can be further controlled, if 1 or two or more interlayers with the presentation in the middle of such two materials are provided between an electrolyte and an air pole and it is made for a presentation to change from an electrolyte to an air pole gradually.

[0038]The material of a desirable fuel electrode is (1). nickel and (2) General formula: It consists of a compound shown by $Ce_{1-m}C_mO_2$ (C means one sort of Sm, Gd, Y, and Ca, or two sorts or more among a formula, and it is m= 0.05-0.4). Both rate, (1) Within the limits of 95:5-20:80 is preferred at the volume ratio of : (2). M value more preferably. It is 0.1-0.3, (1) : (2) Volume ratios are 90:10-40:60.

[0039]The structure in particular of SOFC may not be restricted, cylindrical or a monotonous type may be sufficient as it, and, in a monotonous type case, any of a stack type and an one sintering mold (monolith type) may be sufficient as it. The layered product (one side touches

an air electrode layer and, as for an electrolyte layer, other sides touch a fuel electrode layer) of three layers into which the electrolyte layer was inserted with the air pole and the fuel electrode in any case becomes primitive cell structure. An electrolyte layer is gas impermeability, and each class of an air pole and a fuel electrode is porosity so that gas can be passed. In a cylindrical case, it divides into a cylindrical inside and exterior, fuel gas (an example, hydrogen) and air (or oxygen) are supplied independently, and many cylindrical cells are connected to it via the interconnector provided in a part of the outside surface. In a monotonous type case, gas is supplied using the interconnector of in general a plate type which provided the channel which can supply fuel gas and air independently. This interconnector is accumulated [the monotonous type cell and by turns] which consist of the above-mentioned laminated structure of three layers, and it is multilayered.

[0040]:$1/2O_2$+ which is ionization of oxygen in the air pole one of the reactions which become rate-limiting by the electrode reaction of SOFC is indicated to be with a following formula Since the reaction of $2e^-$ ->O^{2-} ** occurs by the interface of an air pole, an electrolyte, and air, reacting weight increases, so that the area of this interface is large. Therefore, it not being monotonous and, using the above-mentioned three-tiered structure thing as a wave type for example, has so far been performed.

[0041]In the suitable mode of this invention, as shown in drawing 6, unevenness is formed in both sides of an electrolyte layer, and the cellular structure which made the material of the air pole or the fuel electrode adhere to this surface unevenness part in particle state is used. In this case, although it is necessary to make the body part of an electrolyte layer into gas impermeability, the uneven part formed on the surface of both sides may be porosity. the material as an electrolyte with same material of this uneven part (namely, oxide ionic conductor in a narrow sense) it may be -- although -- it is considered as the material in which electronic-ion mixed conductivity is shown preferably. For example, the uneven part by the side of an air pole can consist of oxide ion mixed conductor materials concerning this invention. In that case, as for each particle made to adhere to this uneven part, it is preferred that electron nature electrical conduction like the conventional air pole material consists of dominant materials.

[0042]Such a structure can be formed by baking ion electronic mixed conductor particles first on the surface of an electrolyte layer, making detailed electronic conductor particles adhere by the surface further next, and baking. Or the same structure is realizable at a fixed rate also by making the mixture of ion electronic mixed conductor particles and electronic conductor particles adhere on the surface of an electrolyte layer, and only baking it.

[0043]The material of the conventional air pole has dominant electron nature electrical conduction, such as La(Sr) CoO_3 and La(Sr) MnO_3. (the ion transference number is low) Since

it is an electronic conductor, Even if it ionizes oxygen in the air to oxide ion, it cannot **, if it passes through the inside of air pole material and oxide ion is sent into an electrolyte. Therefore, when using this air pole material, the surface unevenness part by the side of the air pole of drawing 6 is constituted from an electrolyte material, and air pole material is made to adhere to this surface unevenness part in particle state. Ionization of oxygen in that case is drawing 7 (a). It happens only in the one-dimensional field which met the rim (circumference) of the interface of the three phase circuit of an electrolyte layer, air pole particles, and air, i.e., an electrolyte layer and the plane of composition of air pole particles, so that it may be shown. As a result, polarization of an air pole becomes large and the fall of the output of SOFC takes place. Since the electrolyte layer needs to be in contact with air in order to incorporate oxide ion, an air pole cannot cover an electrolyte layer thoroughly, but coating weight also has restriction. Therefore, the electrical link to the external terminal depending on the electron nature electrical conduction of an air pole also becomes imperfect easily. Or in order to obtain sufficient electrical link, the structure of cross linkage which is rich in the opening of the electrical conducting material which covers a three-phase-circuit interface to **, and connects air pole particles is needed, but the opening structure is resisting to passage of gas in that case.

[0044]On the other hand, since the material of the air pole of this invention shows ion electronic mixed conductivity, this material itself can ionize oxygen in the air to oxide ion. Therefore, as mentioned above, the surface unevenness part by the side of the air pole of drawing 6 can be constituted from an oxide ion mixed conductor of this invention, and each particle made to adhere to this uneven part can consist of air pole materials of the conventional electronic conductor. Ionization of oxygen in that case is drawing 7 (b). Since ionization efficiency increases by leaps and bounds since it happens in a two-dimensional field called the surface unevenness part of mixed conductivity material and the whole interface of two phases of air, i.e., the outside surface of this material, and polarization of an air pole can be prevented so that it may be shown, the output of SOFC improves. The oxide ion generated by ionization is transmitted in air pole material by the oxide ion conductivity of this mixed conductivity air pole material, and flows into an electrolyte. In order to help it, the particles of an electronic conductor are made to adhere to the surface of the uneven part by the side of an air pole, although electron nature electrical conduction is also possible for the oxide ion mixed conductor which constitutes this surface unevenness part and the electrical and electric equipment can be sent through an external terminal.

[0045]a fuel electrode -- above -- nickel and ceria system material ($Ce_{1-m}C_mO_2$) from -- constituting is preferred. Also in this case, the ceria system material which is an oxide ion mixed conductor constitutes the surface unevenness part by the side of a fuel electrode, and each particle of that surface consists of nickel which is an electronic conductor. By this

composition, like the case of the air pole mentioned above, delivery of the oxide ion to H_2 is performed in a two-dimensional field, and the efficiency of an H_2O generation reaction improves remarkably too.

[0046]The oxide ion mixed conductor of this invention can be used also as a gas separation membrane. An electron flows into a counter direction at the same time oxide ion will move the inside of membranous toward the low concentration side from the high concentration side for a concentration gradient, if the gas which is two kinds from which oxygen concentration differs is contacted on both sides of this gas separation membrane. As a result, since oxygen flows in the one direction, it functions as a deoxygenation film. This gas separation membrane functions because the electron with which the flow of oxide ion is compensated electrically flows. Therefore, in addition to oxide ion conductivity, electron nature electrical conduction also needs to be shown and especially oxide ion mixed conductor material is suitable.

[0047]This gas separation membrane is applicable also to decomposition of water or NO_X not only in oxygen, for example. Since a difference is made to oxygen ion concentration on membranous both sides, this will serve as driving force, the flow of oxide ion will be made and hydrogen will remain, without flowing if it decomposes into oxygen ion and hydrogen on the surface of a demarcation membrane in the case of water, hydrogen can be manufactured from water. Also in NO_X, it decomposes, NO_X is detoxicated and it separates into nitrogen and oxygen.

[0048]The oxide ion mixed conductor of this invention is still more useful also for the use of the thin film electrode of the electrode of a solid oxide type gas sensor, the negative pole of a gas discharge type display panel, the element for solid oxide type emission gas purification, and a thin film capacitor, etc.

[0049]A solid oxide type gas sensor comprises a solid electrolyte layer which provided the electrode in both sides, The electromotive force or current by the ionic diffusion produced when both sides of this solid electrolyte layer have density difference of gas can be measured by an electrode, and it can constitute as indicated to JP,4-298240,A. With the above-mentioned gazette, it is an electrode layer General formula:$La_{1-x}Sr_xAO_3$ (A) [Co and] perovskite type oxide which has one sort of Cu, Fe, Mn, and nickel, or two sorts or more 0.1 - 50wt% -- desirable -- Although 0.5 - 30wt% and the remainder form from the constituent which consists of platinum, It is a general formula (a) of this invention instead of this perovskite type oxide. A gas sensor is producible like the above-mentioned gazette using the material shown. It is possible to reduce the content of expensive platinum required for conductive reservation in this invention, since the conductivity of a perovskite type oxide is high.

[0050]The ion transference number of the perovskite type oxide material currently used for the electrode of many existing gas sensors is 0.1. It is a grade, and as compared with the material

of this invention, it is dramatically low, and close to an electronic conductor. On the other hand, general formula (a) of this invention Since the ion transference number is high, the perovskite type oxide material shown is preferred as an electrode material of a gas sensor. It replaces with YSZ etc. which are more generally than before used as a solid electrolyte, and is the above-mentioned general formula (b) like the electrolyte of SOFC. The perovskite type oxide shown may be used.

[0051]A gas discharge type display panel is a light-emitting display using gas discharge, it estranges and it arranges the glass plate of two sheets which provided the negative pole or the anode, respectively so that the negative pole and the anode may counter, and it is made to carry out gas discharge in the closed space in it. A mixture with the material of high resistance can be used from this with a perovskite type oxide conductor as a cathode material as indicated by JP,4-366523,A and the 5-74352 **** gazette. It is a general formula (a) of this invention as a perovskite type oxide of this cathode material. Except using the material shown, a gas discharge type display panel is producible according to the statement of the above-mentioned gazette.

[0052]The element for solid oxide type emission gas purification is indicated by JP,9-299749,A. This element has the structure which formed the electrode in both sides of a solid electrolyte layer, and formed the thin film of the perovskite type oxide on the cathode terminal further. It is a general formula (a) of this invention about the thin film of this perovskite type oxide. Except for the point formed from the material shown, the element for emission gas purification is producible like the above-mentioned gazette.

[0053]General formula (a) of this invention Since the material shown has the high ion transference number, on a cathode electrode surface, ionization is promoted further. Therefore, compared with publicly known material, the more highly efficient element for solid oxide type emission gas purification can be manufactured. It replaces with general YSZ etc. as a solid electrolyte layer, and is the above-mentioned general formula (b). The perovskite type oxide shown may be used.

[0054]A thin film capacitor is a dielectric film. (generally it consists of perovskite die materials) It has the structure which sandwiched the upper and lower sides with the thin film electrode. Constituting at least one side of these two thin film electrodes from a perovskite type conductive material is indicated by JP,9-139480,A. At least one thin film electrode can be carried out like a statement in the above-mentioned gazette except for the point constituted from material of this invention, and a thin film capacitor can be produced. In the above-mentioned gazette, it is a general formula (a) of this invention. Using the material shown for a thin film electrode is not specifically shown.

[0055]

[Example](Reference example 1) Each powder of La_2O_3, $SrCO_3$, and Fe_2O_3 (all are not less

than 99% of purity) It mixed at a rate which produces prescribed composition, and preliminary calcination of the powder mixture was carried out at 1100 ** among the air for 6 hours. The sintered compact with the presentation which grinds the mixture which carried out preliminary calcination, carries out compression molding to the shape of a disk of thickness 0.5 mm and diameter 15 mm with a hydrostatic pressure press, calcinates a Plastic solid at 1500 ** among the air for 3 hours, and is shown by $La_{1-x}Sr_xFeO_3$ was obtained. When the crystal structure of the obtained sintered compact was investigated according to the X diffraction, the Perovskite type crystal structure was shown and another phase was not accepted.

[0056]The conductivity of this sintered compact in the rectangular parallelepiped sample cut from the sintered compact of the disk form. A platinum wire is connected after applying the platinum paste used as an electrode. It prints for 10 to 60 minutes at 950-1200 **, It asked within the device which can control oxygen tension and temperature by measuring resistance by direct-current four-poles or an exchange one terminal pair network method in oxygen tension 10^{-5} atm and temperature 800 **. Adjustment of oxygen tension was performed using O_2-N_2, CO-CO_2, and H_2-H_2O mixed gas, and oxygen tension was measured with the YSZ oxygen sensor. A measurement result is as having been shown in drawing 1, and it turns out that conductivity increases remarkably by addition of Sr.

[0057]In oxygen and another side, one side of the atmosphere of the both ends of a sample makes hydrogen the ion transference number of the above-mentioned sintered compact by partition, produce the H_2-O_2 cell which is an oxygen concentration cell, and measure the electromotive force of this cell by 800 **, and. The theoretical electromotive force of the conditions was computed from the Nernst equation, and it asked as a ratio of the measured value/theoretical value of electromotive force. In this way, the ion transference number for which it asked is as having been shown in drawing 2. As already explained in the top, the ion transference number is 0.1 as x value is 0.5 less or equal. It turns out that it becomes the above and becomes an oxide ion mixed conductor.

[0058](Example 1) The sintered compact shown by $La_{0.9}Sr_{0.1}Fe_{1-y}M_yO_3$ (M is Mg, Cr, aluminum, Co, Mn, Ga, Cd, and Ag) was produced like the reference example 1. When the crystal structure of the obtained sintered compact was investigated according to the X diffraction, the Perovskite type crystal structure was shown and another phase was not accepted.

[0059]The result of having measured the conductivity of this oxide sintered body on the conditions like the reference example 1 is shown in drawing 3. According to this invention, it turns out that the material whose M is Mg, Cr, aluminum, or Ga can raise conductivity remarkably at addition of a little M elements.

[0060](Example 2) The sintered compact shown by $La_{0.9}Sr_{0.1}Fe_{0.9}M_{0.1}O_3$ (M uses the oxide of not less than 99% of the purity of each metal as Mg, Cr, aluminum, CoMn, Ga, Cd, Ag, and a raw material) was produced like Example 1. It is a relation with the reciprocal of temperature about the result of having changed temperature and having measured the conductivity of this oxide sintered body by oxygen tension 10^{-5} atm like the reference example 1. (Arrhenius plot) It carries out and is shown in drawing 4. even if the material of this invention has the dramatically small temperature dependence of conductivity and temperature changes, it turns out that the conductivity carried out about 1 law is shown.

[0061]The result of having measured the ion transference number of this material like the reference example 1 is shown in drawing 5. As for the ion transference number, although it changes with temperature, the ion transference number is 0.1 at the temperature more than 500 - 600 **. It turns out that it becomes the above oxide ion mixed conductor.

[0062]

[Effect of the Invention]The oxide ion mixed conductor concerning this invention which shows both electron nature electrical conduction and the ionicity electrical conduction by oxide ion, 600 the wide temperature requirement which ranges below from ** to not less than 1000 ** shows the high conductivity carried out about 1 law -- this temperature requirement -- the ion transference number An action is carried out as an oxide ion mixed conductor of 0.1-0.3.

[0063]This oxide ion mixed conductor is useful as an air pole material of a solid oxide type fuel cell, and, thereby, the reduction and improved efficiency of the manufacture cost of this kind of fuel cell of it become possible. This material is useful as gas separation membranes, such as an air separation film, and can be further used for a solid oxide type gas sensor, a gas discharge type display panel, the element for solid oxide type emission gas purification, etc. as an electrode material etc.

[Translation done.]